Synchrotron radiation-based Mössbauer spectra of ^{174}Yb measured with internal conversion electrons

Mössbauer spectroscopy is a well-established method in physics, chemistry, biology, and earth science, since it provides element-specific information on the electronic states, such as valence and magnetism in complex materials. Most Mössbauer studies are performed using ^{57}Fe and ^{119}Sn with radioactive isotopes (RI) sources, although the Mössbauer effect has been observed in approximately 100 nuclides of nearly 50 elements (See Fig. 1). One major difficulty in Mössbauer spectroscopy is preparation of RI as γ-ray sources, but this can be avoided using synchrotron radiation (SR); we can select X-rays with the appropriate energy for the Mössbauer effect. Moreover, SR has high brilliance and thus the electronic states can be studied under extreme conditions like high pressure. SR-based Mössbauer spectroscopy developed in 2009 is one such method in the energy domain [1], and measurements using many nuclides are promising (Fig. 1). In fact, ^{151}Eu Mössbauer study has already been performed under high pressure with this method [2]. However, the measurements are often time consuming. To reduce the measurement time, we aimed to enhance the counting rate of the emission from the nuclear excited state. From the nucleus resonantly excited, γ-rays or internal conversion (IC) electrons are emitted at the de-excitation. In previous measurements, the IC electrons were not detected, while the γ-rays or the fluorescent X-rays that accompany the IC electron emission were detected, because the X-ray windows of the cryostat and the detector shield the electrons. Therefore, we developed a detection system using an X-ray-windowless avalanche photodiode (APD) detector and a sample chamber with a He-flow cryostat [3]. The developed system is applicable to SR-based Mössbauer spectroscopy for the 76.5 keV excited state of ^{174}Yb. ^{174}Yb is the most abundant Yb nuclide (natural abundance of 31.4%), but is not the most popular for Yb Mössbauer spectroscopy due to difficulties in preparing its RI source [4]. If ^{174}Yb Mössbauer spectroscopy is possible, then expensive isotope enrichment is unnecessary.

The experimental setup for SR-based Mössbauer spectroscopy is shown in Fig. 2. The experiments were performed at beamlines **BL09XU** and **BL11XU**. The electron-storage ring's operating mode was the "203 bunch" mode. SR with the energy of the ^{174}Yb nuclear resonance was transmitted by a sample in the cryostat (the "transmitter" in Fig. 2). Then the SR was scattered by a sample in another cryostat (the "scatterer" in Fig. 2). The scatterer was moved using a velocity transducer to measure the Mössbauer spectrum at low temperatures. In the cryostat, an eight-element APD detector was combined to its flange on one side (Fig. 2 upper right) and arranged just above the scatterer under vacuum, so that electrons can reach the detector. Thus, both the emitted IC electrons and X-rays from the scatterer can be detected with the APD. Because nuclear resonant scattering (NRS) by ^{174}Yb is emitted with a delay (half-life $t_{1/2}$=1.79 ns), NRS was counted in the time window between 6.1 ns and 13.6 ns after the SR incidence. In this system, either the transmitter or the scatterer is studied, while the other is used as the energy standard. In this study, both the transmitter and scatterer were natural YbB_{12} powdered from a single crystal [5] because the large recoilless fraction of YbB_{12} is advantageous when observing a clear signal in the Mössbauer spectrum. The transmitter thickness was 60.9 mg/cm^2 YbB_{12}, while that of the scatterer was 736 mg/cm^2 YbB_{12}. The transmitter was set to 20 K and the scatterer was set to 26 K in a <0.01 Pa vacuum.

The ^{174}Yb Mössbauer spectrum observed within 10 hours is shown in Fig. 3. The NRS counting rate was 6 cps, while it was 1.2 cps in our previous ^{174}Yb SR-based Mössbauer spectroscopy using an eight-element APD with an X-ray window. Therefore, the counting rate was five times higher than that of the previous system. The spectrum was evaluated using the formulae in Ref. 1. Here, absorption spectrum

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	104~														
*Lanthanide		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
**Actinide		Ac	Th	Pa	U	Np	Pu	Am	Cm		Cf	Es	Fm	Md	No	Lr	

Elements including Mössbauer active nuclide
Elements without Mössbauer active nuclide

Fig. 1. Table of elements including Mössbauer active nuclides.

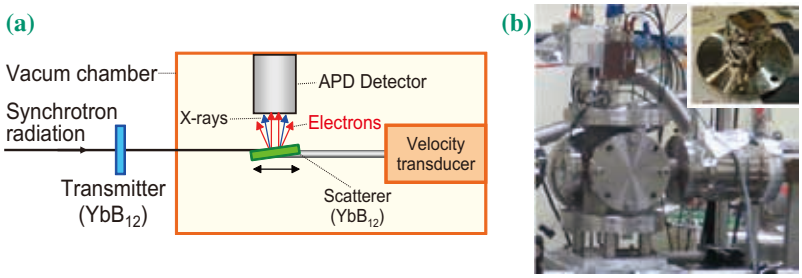

Fig. 2. **(a)** Schematic drawing of the developed X-ray windowless system for the SR-based Mössbauer spectroscopy, **(b)** photo of the vacuum chamber, and (**inset** in **b**) the X-ray windowless APD detector.

narrows owing to the time window, which leads to an improved spectrum resolution. The full width at half maximum (FWHM) of this spectrum is 1.3 ± 0.2 mm/s. Because the narrowest ideal width in conventional RI Mössbauer spectroscopy is 2.0 mm/s at FWHM for the nuclear level of ^{174}Yb, the FWHM of the observed spectrum is narrower than the conventional ideal width. In some cases, this narrowing effect is useful to experimentally determine the energy shifts in Mössbauer spectra; the difference in isomer shifts between Yb^{2+} and Yb^{3+} is less than 0.2 mm/s in the ^{174}Yb spectrum, and consequently, the line width is critical.

The detection system developed here can also be applied to the SR-based Mössbauer spectroscopy using other nuclides. In fact, many nuclides in Fig. 1 also have high IC coefficients, and this system should realize drastic improvement of the counting rates in Mössbauer spectroscopy with these nuclides. Especially, rare-earth elements except Ce have Mössbauer active nuclides with high IC coefficients. Therefore, the SR-based Mössbauer spectroscopy using this system should be utilized to study the electronic states (especially 4*f*) of the rare-earth compounds.

In summary, the IC electron detection system developed here dramatically enhances the counting rate in SR-based Mössbauer spectroscopy enabling efficient measurements. ^{174}Yb Mössbauer spectroscopy was performed using this system, and a fivefold increase in the counting rate of NRS of SR by ^{174}Yb is achieved. As a result, the spectrum of YbB_{12} can be measured within 10 hours without ^{174}Yb enrichment. Because ^{174}Yb has the largest natural abundance of Yb nuclides (31.8%), a specially enriched sample does not need to be prepared for Yb Mössbauer spectroscopy. The Mössbauer spectrum in the energy-domain is applicable to complex materials. Hence, our system should allow for efficient measurements in a wide variety of scientific areas using the various nuclides including ^{174}Yb.

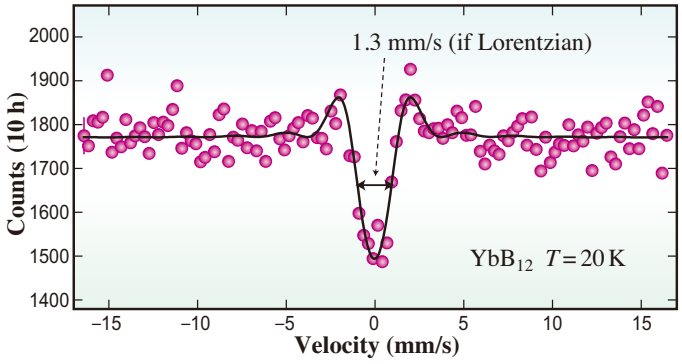

Fig. 3. ^{174}Yb SR-based Mössbauer spectrum of YbB_{12}. Circles and curved line are experimental data and fit using the formulae in Ref. 1, respectively.

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